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Coupling of Optic and Acoustic Modes of Vibration in Crystals

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Ernest Bauer

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Morris Kline
Project Director
September, 1956

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Abstract

The transition probability for transfer of energy from one optic to two or three acoustic modes of vibration has been calculated for NaCl, and found to be of the order 10^{12} per sec at low temperatures.

I. Introduction

In a crystalline solid, the atoms oscillate about their mean positions on the regular crystal lattice. At not too high temperatures, these oscillations may be considered to be harmonic. In this case, if we Fourier analyze the displacement from equilibrium of all the atoms in a given crystal, we can describe the 3N degrees of freedom of N atoms in terms of 3N Fourier components or 'lattice vibrations'. These components represent the thermal motion of the system in terms of vibrations of the crystal lattice as a whole. (Strictly speaking, there are 3N-5 such modes, if we eliminate the motion of the center of mass of the system as a whole, and any rotation about some space direction.) In practice, following Born and von Karman[1], one imposes the 'cyclic boundary conditions' to limit the number of acceptable lattice vibrations to 3N. This may be regarded[2], [3] as a device for obtaining a complete set of lattice vibrations in terms of which to describe the motion. Use of the cyclic boundary conditions is certainly permissible if N is sufficiently large, and if we study phenomena that do not depend critically on the surface of the crystal.

The lattice vibrations in a polyatomic crystal are of two types, namely acoustic modes, which correspond to translation of the atoms or molecules in a gas, and optic modes, which correspond to internal molecular vibrations and rotation. (Thus there can be no optic modes in a monatomic crystal like Na or Ne.) The relation between frequency $\omega/2\pi$ and wave number $k/2\pi$ for these two types of motion is shown in Fig. 1 for a typical linear (one-dimensional) lattice. In a three-dimensional lattice there will be several optic and acoustic branches, while the limiting wave number k_M will in general be different for different directions in the crystal.

The existence of these lattice vibrations as stationary states of the system is an immediate consequence of the harmonic character of the oscillation of the individual atoms about their equilibrium positions. In fact these oscillations are not strictly harmonic, and thus the description of the thermal motion of the crystal in terms of lattice vibrations is not an exact one, though it is a very satisfactory description within its limitations. If we expand the potential energy of an atom in powers of the displacement from its equilibrium position in the lattice, and go beyond the quadratic (harmonic) term to cubic and perhaps quartic terms in the displacement, we find that a number of new physical effects can be explained, such as a non-zero thermal expansion, a finite thermal conductivity, and the possibility of a rise in the specific heat above its equipartition values at sufficiently high temperatures.

If we take into account these anharmonic terms and still try to describe the motion of the atoms of the crystal in terms of lattice vibrations, these modes are now no longer stationary states of the system, since the anharmonic terms in the potential energy induce transitions between the various modes. Such a mechanism is invoked in the explanation of the thermal conductivity of ionic crystals[2], [3], for example. In particular, by reference to Fig. 1 we see that the coupling of optic and acoustic modes of vibration in a solid is the analog of the excitation and de-excitation of molecular vibrations by collisions in a gas. A specific application of this process is to the calculation of the rates of various chemical reactions[4]. In the present paper we calculate the transition probability governing the flow of energy between optic and acoustic modes of vibration in a crystal as a starting point from which it might ultimately be possible to attempt to calculate the rates of certain chemical reactions in liquids.

For simplicity and definiteness we shall here consider the case where

$$\omega_o < 2\omega_M , \qquad (1)$$

so that an optic mode can split up into two acoustic modes. We shall also consider the transition into three acoustic modes. This means that we could apply the present considerations to NaCl, for instance, and we do in fact use NaCl for the present order-of-magnitude calculations. However, it must be stressed that the present calculations are schematic, and should not be applied too literally to any given substance.

2. Harmonic approximation

We consider a crystal containing 2N atoms, N of each of two chemical species A and B, in a regular array. The displacements of these atoms from their equilibrium positions will be denoted by $\underline{u}_{j,\underline{n}}$, where $j = A, B$ for the A and B atoms in a given basic cell which is labeled by $\underline{n} = (n_x, n_y, n_z)$. There are thus N cells each of volume Ω_c, the $\underline{n}$-th cell being located at $\underline{d}_{\underline{n}}$. Now we expand $\underline{u}_{j,\underline{n}}$ in terms of a set of normal coordinates $q_{\underline{k},s} = q_{\underline{k},s}(t)$; we get

$$(2) \qquad \underline{u}_{j,\underline{n}} = \frac{1}{N^{1/2}} \sum_{\underline{k},s} q_{\underline{k},s}\, e^{i\,\underline{k}\cdot\underline{d}_{\underline{n}}}\, \underline{v}_j(\underline{k},s) .$$

Here $\underline{v}_j(\underline{k},s)$ is a unit polarization vector; s = opt., acoust., corresponding to the respective modes, and the summation over the wave vectors $\underline{k}$ extends over all points inside the first Brillouin zone. Note that our normal coordinate $q_{\underline{k},s}$ has been defined with the dimension of length, not $(\text{mass})^{1/2}$ x (length); in this we are following the convention in this field[2], [3] .

The potential energy of the lattice in harmonic approximation is given by

$$(3) \quad \begin{aligned} &(a) \quad V = V^{(o)} + V^{(2)} \\ &(b) \quad V^{(o)} = \text{constant} \\ &(c) \quad V^{(2)} = (1/2!) \sum_{j,j'} \sum_{\underline{n},\underline{n}'} \underline{A}_{j\underline{n};j'\underline{n}'}\, \underline{u}_{j\underline{n}}\, \underline{u}_{j'\underline{n}'} , \end{aligned}$$

where

$$(4) \qquad \underline{A}_{j\underline{n};j'\underline{n}'} = \underline{A}_{jj'}(\underline{d}_{\underline{n}} - \underline{d}_{\underline{n}'}) = \underline{A}_{jj'}(\underline{d}_{\underline{n}'} - \underline{d}_{\underline{n}}),$$

since the potential energy depends only on the relative orientation of the cells in the lattice[2].

With the transformation (2), we find that

$$(5)\quad \begin{cases} \text{(a)} \quad V^{(2)} = \frac{1}{2} \sum_{\underline{k},s} M_s \left[\omega(\underline{k},s)\right]^2 q^*_{\underline{k},s}\, q_{\underline{k}s} \\ \text{(b)} \quad M_{\text{acoust}} = M_A + M_B ; \quad M_{\text{opt}} = M_A M_B \big/ (M_A + M_B) , \end{cases}$$

where $\omega(\underline{k},s)$ is the (angular) frequency of the $(\underline{k},s)$ mode and is given by a root of the secular equation

$$(6)\qquad \det \left\{ \delta_{jj'} M_j \left[\omega(\underline{k},s)\right]^2 + \sum_{\underline{n}} A_{jj'}(\underline{d}_{\underline{n}})\, e^{i\underline{k}\cdot\underline{d}_{\underline{n}}} \right\} = 0 ; \quad j = A,B.$$

In the present case of a diatomic lattice, the secular equation is a 2 x 2 determinant, having two solutions $\omega(\underline{k},s)$ for each of the 3N values of $\underline{k}$ lying in the first Brillouin zone; these two solutions correspond to s = opt., acoust. The problem of solving (6) to give the functional form of $\omega(\underline{k},s)$ and of the frequency spectrum of the lattice vibrations was first discussed by Born and von Karman[1]; for any specific case it generally leads to very lengthy calculations. Here we shall use the simplest possible approximation, of the 'Debye-Einstein' form (cf. Fig. 1):

$$(7)\quad \begin{cases} \text{(a)} \quad \text{Optic branch:} \quad \omega = \omega_0 , \quad \text{independent of } \underline{k}, \quad |\underline{k}| \leq k_M \\ \text{(b)} \quad \text{Acoustic branch:} \quad \omega = c_A |\underline{k}|, \quad |\underline{k}| \leq k_M ; \quad c_A = \text{sound velocity.} \end{cases}$$

Physically, the Einstein form (7a) for the optic branch corresponds to a situation where the internal molecular vibration is only weakly coupled with the 'external' or translational motion. It is a good approximation for a diatomic lattice with very different masses of the two ions; in this case, however, $\omega_0 \gg \omega_M = c_A k_M$. The Debye form (7b) for the acoustic branch is derived on the assumption of a continuum, with no characteristic atomic structure. We see thus that the present form of the relation between ω and $\underline{k}$ is not particularly adequate; however, it is certainly a proper form to take for an exploratory calculation like the present one, because any more satisfactory form will entail much more labor in the calculation.

3. Anharmonicity

If we take third and fourth order terms in the potential energy into account, (3a) must be replaced by

$$
(8)\left\{
\begin{array}{ll}
\text{(a)} & V = V^{(0)} + V^{(2)} + V^{(3)} + V^{(4)} + \cdots \\[2ex]
\text{(b)} & V^{(3)} = \left(\frac{1}{3!}\right) \sum_{jj'j''} \sum_{\underline{n}\,\underline{n}'\underline{n}''} B_{j\underline{n};j'\underline{n}';j''\underline{n}''}\, \underline{u}_{j\underline{n}}\, \underline{u}_{j'\underline{n}'}\, \underline{u}_{j''\underline{n}''} \\[2ex]
\text{(c)} & V^{(4)} = \left(\frac{1}{4!}\right) \sum_{jj'j''j'''} \sum_{\underline{n}\,\underline{n}'\underline{n}''\underline{n}'''} C_{j\underline{n};j'\underline{n}';j''\underline{n}'';j'''\underline{n}'''} \\
 & \qquad\qquad \underline{u}_{j\underline{n}}\, \underline{u}_{j'\underline{n}'}\, \underline{u}_{j''\underline{n}''}\, \underline{u}_{j'''\underline{n}'''}\,.
\end{array}
\right.
$$

If we transform $V^{(3)}$ and $V^{(4)}$ by (2), we find that

$$
(9)\left\{
\begin{array}{ll}
\text{(a)} & V^{(3)} = \left(\frac{1}{3!N^{1/2}}\right) \sum_{\underline{k}s;\underline{k}'\underline{s}';\underline{k}''s''} b(\underline{k}s;\underline{k}'s';\underline{k}''s'')\, q_{\underline{k}s}\, q_{\underline{k}'s'}\, q_{\underline{k}''s''} \\[2ex]
\text{(b)} & V^{(4)} = \left(\frac{1}{4!N}\right) \sum_{\underline{k}s;\underline{k}'s';\underline{k}''s'';k'''s'''} c(\underline{k}s;\underline{k}'s';\underline{k}''s'';\underline{k}'''s''')\, q_{\underline{k}s}\, q_{\underline{k}'s'} \\
 & \qquad\qquad q_{\underline{k}''s''}\, q_{\underline{k}'''s'''},
\end{array}
\right.
$$

where

$$
(10)\left\{
\begin{array}{ll}
\text{(a)} & b(\underline{k}s;\cdots) = \frac{1}{N} \sum_{j\underline{n};j'\underline{n}';j''\underline{n}''} B_{j\underline{n};j'\underline{n}';j''\underline{n}''}\, \underline{v}_j(\underline{k}s)\, \underline{v}_{j'}(\underline{k}'s')\, v_{j''}(\underline{k}''s'') \\
 & \qquad\qquad \exp\left[i \left\{ \underline{k}\cdot\underline{d}_{\underline{n}} + \underline{k}'\cdot\underline{d}_{\underline{n}'} + \underline{k}''\cdot\underline{d}_{\underline{n}''} \right\} \right] \\[2ex]
\text{(b)} & c(\underline{k}s;\cdots) = \frac{1}{N} \sum_{j\underline{n};\cdots j'''\underline{n}'''} C_{j\underline{n};\cdots j'''\underline{n}'''}\, \underline{v}_j(\underline{k}s) \cdots \underline{v}_{j'''}(\underline{k}'''s''') \\
 & \qquad\qquad \exp\left[i \left\{ \underline{k}\cdot\underline{d}_{\underline{n}} + \cdots + \underline{k}'''\cdot\underline{d}_{\underline{n}'''} \right\} \right] .
\end{array}
\right.
$$

By consideration of the crystal symmetry it can be shown[2], [3] that $b(\underline{k}s;\underline{k}'s';\underline{k}''s'')$ and $c(\underline{k}s;\underline{k}'s';\underline{k}''s'';\underline{k}'''s''')$ differ from zero only if

$$(11)\quad \begin{cases} \text{(a)}\quad \underline{k} + \underline{k}' + \underline{k}'' = 0 \text{ or } \underline{K}, \text{ a vector in the 'reciprocal lattice'} \\ \text{(b)}\quad \underline{k} + \underline{k}' + \underline{k}'' + \underline{k}''' = 0 \text{ or } \underline{K}. \end{cases}$$

Further, $b(\underline{k}s;\ldots)$, $c(\underline{k}s;\ldots)$ as defined in (10) are independent of N, that is, of the total size of the crystal.

It is rather difficult to visualize the precise meaning of (10), and so we shall present a simple model as an illustration, namely a monatomic linear lattice consisting of N identical particles spaced on a line with mean interatomic separation d. If the interaction between two particles distant $x = nd + u_n$ is $\phi(x)$, then if we expand $\phi(x)$ in a Taylor series about nd, we get

$$(12)\quad \begin{cases} \text{(a)}\quad V = V^{(o)} + V^{(2)} + V^{(3)} + V^{(4)} + \ldots \\ \text{(b)}\quad V^{(o)} = \text{constant} \\ \text{(c)}\quad V^{(2)} = \frac{1}{2} \sum_{n=1}^{N} \sum_{m=1}^{N'} \phi''(md)\left(\frac{1}{2!}\right)\left[(u_{n+m}-u_n)^2 + (u_n-u_{n-m})^2\right] \\ \text{(d)}\quad V^{(3)} = \frac{1}{2} \sum_{n=1}^{N} \sum_{m=1}^{N'} \phi'''(md)\left(\frac{1}{3!}\right)\left[(u_{n+m}-u_n)^3 + (u_n-u_{n-m})^3\right] \\ \text{(e)}\quad V^{(4)} = \frac{1}{2} \sum_{n=1}^{N} \sum_{m=1}^{N'} \phi''''(md)\left(\frac{1}{4!}\right)\left[(u_{n+m}-u_n)^4 + (u_n-u_{n-m})^4\right]. \end{cases}$$

We wish to transform u_n to normal coordinates q_k; then

$$(13)\qquad u_n = \frac{1}{N^{1/2}} \sum_k q_k\, e^{iknd}\, v_k .$$

(Note that $v_k = 1$ in the present case.) Let us suppose that each particle only interacts with its nearest neighbors, i.e., $m = N' = 1$. This simplifies the argument, but does not impose any restriction on it. The cubic term is now

$$(14)\quad \begin{cases} V^{(3)} = \dfrac{\phi'''(d)}{2\cdot 3!} \sum_{n=1}^{N} \sum_{kk'k''} v_k v_{k'} v_{k''} q_k q_{k'} q_{k''} e^{i(k+k'+k'')nd} \\ \qquad \left\{ (e^{ikd}-1)(e^{ik'd}-1)(e^{ik''d}-1) + (1-e^{-ikd})(1-e^{-ik'd})(1-e^{-ik''d}) \right\}. \end{cases}$$

Now carry out the sum over n. We use the result[2], [3]

$$(15)\quad \sum_{n=1}^{N} e^{ifnd} = \begin{cases} N & \text{if } fd = 0 \text{ or } 2\pi x \text{ (an integer)} \\ 0 & \text{otherwise}, \end{cases}$$

which is precisely the origin of condition (11). In this way we get

$$(16)\quad \begin{cases} V^{(3)} = \dfrac{\phi'''(d)}{2\cdot 3!N^{1/2}} \sum_{kk'k''} v_k v_{k'} v_{k''} \Big\{ (e^{ikd}-1)(e^{ik'd}-1)(e^{ik''d}-1) \\ \qquad\qquad + (1-e^{ikd})(1-e^{ik'd})(1-e^{ik''d}) \Big\} q_k q_{k'} q_{k''} \\ \quad = \dfrac{1}{3!N^{1/2}} \sum_{kk'k''} b(k,k',k'') q_k q_{k'} q_{k''}, \end{cases}$$

where the only contribution comes from terms in the sum satisfying the condition

$$(17a)\quad k + k' + k'' = 0 \quad \text{or} \quad 2\pi x \text{ (an integer)} \quad (\text{'reciprocal lattice'}).$$

Similarly,

$$(18)\quad \begin{cases} V^{(4)} = \dfrac{1}{4!N} \sum_{kk'k''k'''} c(k,k',k'',k''') q_k q_{k'} q_{k''} q_{k'''} \\ c(k,\ldots,k''') = \dfrac{\phi'''(d)}{2} v_k v_{k'} v_{k''} v_{k'''} \Big\{ (e^{ikd}-1)\cdots(e^{ik'''d}-1) \\ \qquad\qquad + (1-e^{-ikd})\cdots(1-e^{-ik'''d}) \Big\}, \end{cases}$$

where the only contribution to the sum over k's comes from terms satisfying

$$(17b)\quad k + k' + k'' + k''' = 0 \quad \text{or} \quad 2\pi x \text{ (an integer)} \; (\text{'reciprocal lattice'}).$$

It is clear that the present argument can be extended to any order of neighbor interaction, N', by going through the present analysis for m = 2, 3, ... successively, and we can also extend it to three dimensions.

An estimate of the order of magnitude of $b(\underline{k}s;\underline{k}'s';\underline{k}''s'')$ can be made by using Klemens' result[5]. For three acoustic modes A, A', A'' he gives the estimate

$$(18) \qquad b(A;A';A'') = 4\sqrt{3}\ M_{acoust}\ \gamma\ \frac{\omega_A \omega_{A'} \omega_{A''}}{c_A} ,$$

where γ is the Grueneisen constant[3] defined by

$$(19) \qquad \gamma - \frac{d \ln \omega}{d \ln V}$$

which equals approximately 2, for most materials. The result (18) disregards specific crystal structure and polarization effects. A plausible generalization of this to the present case where we want $b(O;A1;A2)$ would be

$$(20) \qquad b(O;A1;A2) \cong (8/\sqrt{3})\ (M_{opt} M_{acoust}^{2})^{1/3}\ \gamma\ \omega_o \omega_{A1} \omega_{A2} / c_A .$$

It is even more difficult to give an estimate of the quartic potential coefficient, $c(O;A1;A2;A3)$. On purely dimensional considerations we shall put

$$(21) \qquad \frac{c(O;A1;A2;A3)}{b(O;A1;A2)} \sim \frac{\alpha}{d} ,$$

where α is probably in the range

$$(22) \qquad 0.1 \lesssim \alpha \lesssim 10.$$

4. Phonon-phonon collisions: general discussion

We are concerned here with transitions in which an optic phonon O, of frequency ω_o and wave number $\underline{k}_o$, goes into either two or three acoustic phonons A1, A2, A3 of frequency ω_{A1}, ω_{A2}, ω_{A3} and wave number $\underline{k}_{A1}$, $\underline{k}_{A2}$, $\underline{k}_{A3}$. Thus, we wish to discuss the two-phonon process II:

$$\text{(23)} \qquad \text{Process II:} \qquad O \Longrightarrow A1 + A2,$$

which can be produced by the cubic potential $V^{(3)}$, and also the three-phonon process III:

$$\text{(24)} \qquad \text{Process III:} \qquad O \Longrightarrow A1 + A2 + A3,$$

which can be produced either by the quartic potential $V^{(4)}$, or by successive application of $V^{(3)}$. 'Graphs' of the possible mechanisms of these transitions are shown in Fig. 2.

In studying a given transition, one always has to examine the conditions of conservation of energy and momentum. For processes II, III these are

$$\text{(25)} \qquad \begin{cases} \text{II:} & \omega_o = \omega_{A1} + \omega_{A2} \\ \text{III:} & \omega_o = \omega_{A1} + \omega_{A2} + \omega_{A3}, \end{cases}$$

$$\text{(26)} \qquad \left.\begin{cases} \text{II:} & \underline{k}_o - (\underline{k}_{A1} + \underline{k}_{A2}) \\ \text{III:} & \underline{k}_o - (\underline{k}_{A1} + \underline{k}_{A2} + \underline{k}_{A3}) \end{cases}\right\} = 0 \text{ or } \underline{K}, \text{a vector in the reciprocal lattice.}$$

Notice that on account of the periodic structure of the lattice, momentum has only to be conserved modulo a vector $\underline{K}$ of the reciprocal lattice; processes with $\underline{K} \neq 0$ are called 'Umklapp' processes [2], [3].

In calculating the transition probability for a given process, we use the quantum mechanical rather than a classical description, and in particular, we use a field theoretical description [2], [3], [6] which is convenient and well known.

Thus we need the transition matrix elements for these processes.

The transition matrix element for process II is

$$(27)\quad V'_{II} = (F|V^{(3)}|0) = (\hbar/2)^{3/2}\,\frac{b(0;A1;A2)}{3!\,N^{1/2}}\left[\frac{n_o(n_{A1}+1)(n_{A2}+1)}{M_{opt}M^2_{acoust}\omega_o\omega_{A1}\omega_{A2}}\right]^{1/2}$$

where n_o, n_{A1}, n_{A2} are the numbers of phonons of type O, A1, A2 before the collision. Similarly, the transition matrix element for process III is

$$V'_{III} = (F|V^{(4)}|0) + \frac{(F|V^{(3)}|I)(I|V^{(3)}|0)}{E_o - E_1}$$

$$(28)\quad = (\hbar/2)^2\,\frac{\tilde{c}(0;A1;A2;A3)}{4!\,N}\left[\frac{n_o(n_{A1}+1)(n_{A2}+1)(n_{A3}+1)}{M_{opt}M^3_{acoust}\omega_o\omega_{A1}\omega_{A2}\omega_{A3}}\right]^{1/2} ,$$

$$\tilde{c}(0;A1;A2;A3) = c(0;A1;A2;A3) + \frac{2b(0;A1;\bar{A})b(\bar{A};A2;A3)(n_A+1)}{M_{acoust}(\omega_o-\omega_{A1}-\omega_{\bar{A}})\,\omega_{\bar{A}}} .$$

Recall that while momentum is conserved in both steps of the transition IIIB, namely

$$(29)\quad 0 \Longrightarrow A1 + \bar{A} \qquad \text{and} \qquad \bar{A} \Longrightarrow A2 + A3,$$

yet energy is not conserved in the individual steps of (29), though it is of course conserved overall. Thus the energy denominators in (28) do not vanish.

In order to find the transition probability, we still have to find the density of final states per unit energy range. For process II this is

$$(30)\quad \left\{\begin{aligned} d\rho(II)/dE &= \frac{N\Omega_c d^3\underline{k}_{A1}}{(2\pi)^3 dE}\quad \frac{N\Omega_c d\cos\theta_{A1} d\phi_{A1} k^2_{A1}}{(2\pi)^3}\quad \frac{dk_{A1}}{dE} \\ E &= \hbar\left\{\omega(\underline{k}_{A1}) + \omega(\underline{k}_o - \underline{K} - \underline{k}_{A1})\right\} \\ dk_{A1}/dE &= 1\Big/\left\{\hbar\, c_A(1 - \cos\theta_{12})\right\} ,\end{aligned}\right.$$

where θ_{12} is the angle between the vectors $\underline{k}_{A1}$ and $\underline{k}_{A2}$, Ω_c is the volume per unit cell, and c_A the velocity of sound of equation (7b). For process III, if we treat $\underline{k}_{A1}$, θ_{A2}, ϕ_{A2} as independent variables, we have

$$(31)\quad \begin{cases} \dfrac{d\rho(\mathrm{III})}{dE} = \dfrac{N\Omega_c d^3\underline{k}_{A1}}{(2\pi)^3} \; \dfrac{N\Omega_c k_{A2}^2 d\cos\theta_{A2} d\phi_{A2}}{(2\pi)^3} \; \dfrac{dk_{A2}}{dE} \\ \dfrac{dk_{A2}}{dE} = 1 \Big/ \left\{ \hbar c_A (1 - \cos\theta_{23}) \right\} , \end{cases}$$

where θ_{23} is the angle between $\underline{k}_{A2}$ and $\underline{k}_{A3}$.

Now the transition probability per unit time for a given process Λ = II, III is given by the formula

$$(32)\qquad P_\Lambda = (2\pi/\hbar) \textstyle\sum_F |V'_\Lambda|^2 \; d\rho(\Lambda)/dE; \quad \Lambda = \mathrm{II},\ \mathrm{III},$$

where $\sum_F$ denotes summation over all final states consistent with conservation of energy and momentum, that is, integration over $d\cos\theta_{A1}\, d\phi_{A1}$ in case II, and over $d^3\underline{k}_{A1} d\cos\theta_{A2}\, d\phi_{A2}$ in case III. We note that P is a well-defined physical quantity in that it is independent of N, i.e., of the size of the crystal. It does, however, still depend on the magnitude and direction of the incident momentum $\underline{k}_o$. This is partly a genuine effect, but to some extent due to the Einstein form of the frequency spectrum (equation (7a)). At a later stage we shall average the transition probability over all possible incident momenta and also over all possibilities of Umklapp.

5. The two-phonon process II

We wish to make a detailed calculation of the transition probability for process II of equation (23). Let us begin by considering the restrictions imposed by conservation of energy and momentum. Equations (25-II) and (26-II) give four conditions for the six unknown components of $\underline{k}_{A1}$ and $\underline{k}_{A2}$, so that there are two undetermined parameters (which were taken as the two angles θ_{A1}, ϕ_{A1} in the discussion of equation (30)). Clearly $\underline{k}_{A1}$, $\underline{k}_{A2}$ define a plane - say the (xy)-plane; $\underline{k}_o$ lies in that plane, and may be taken to define the x-axis. Thus the azimuth giving the orientation of the (xy)-plane in space is one of our two undetermined parameters. The second parameter is less trivial and more specific to the model, so let us now use the explicit form (7) of the relation between ω and k. If we write $\underline{q}_o$ for $\underline{k}_o$, or for $(\underline{k}_o - \underline{K})$, depending on whether or not there is an Umklapp, then conservation of momentum and energy impose the following requirements on $\underline{k}_{A1}$ and $\underline{k}_{A2}$:

$$(33) \qquad \underline{k}_{A1} + \underline{k}_{A2} = \underline{q}_o \; ; \qquad k_{A1} + k_{A2} = (\omega_o/c_A).$$

Thus, the endpoints of $\underline{k}_{A1}$ and $\underline{k}_{A2}$ lie on an ellipse (strictly speaking, on an ellipsoid of revolution). The situation is shown in Fig. 3, and we see that our second undetermined parameter may conveniently be chosen as $\mu = \cos\alpha$, rather than as $\cos\theta_{A1}$. The ellipse is characterized by its eccentricity

$$(34a) \qquad e = OB/OX = (q_o c_A/\omega_o)$$

and its semi-major axis

$$(34b) \qquad a = OX = \omega_o/2c_A \; .$$

In terms of these we can readily obtain the results

$$(35) \quad \begin{cases} k_{A1} = a(1 + e\mu) \\ \cos\theta_{A1} = \dfrac{e+\mu}{1+e\mu} \\ 1-\cos\theta_{12} = \dfrac{2(1-e^2)}{1-e^2\mu^2} \; . \end{cases}$$

We have to investigate the possibility of Umklapp processes. This is displayed graphically in Fig. 4 for typical values of the magnitudes of $\underline{k}_o$, $\underline{k}_{A1}$, and $\underline{k}_{A2}$. We see that in addition to the 'normal' process, there is just one possible type of Umklapp in the present situation.

Let us now combine equations (30), (32), and write the transition probability for process II as

$$(36) \qquad \partial P_{II}/\partial\mu = \frac{|V'_{II}|^2 N\Omega_c \omega_{A1}^2}{(2\pi)^3 \hbar^2 c_A^3} \frac{\partial\cos\theta_{A1}}{\partial\mu} \frac{1}{1-\cos\theta_{12}} ,$$

where ω_{A1} and hence V'_{II} is regarded as a function of μ through (7), (27), and (35).

We are interested in the total transition probability

$$(37) \qquad P_{II}(\underline{q}_o) = \int_{-m}^{m} \partial P_{II} / \partial\mu \, d\mu \, .$$

Note that in general the limits of integration will not be $-1 \leq \mu \leq 1$. We know that $k_{A1}, k_{A2} \leq k_M$, which gives the limits $-m \leq \mu \leq m$, where

$$(38) \qquad m \doteq \mathrm{Min}\left\{1, \ (1/e)\ (2\omega_M/\omega_o - 1)\right\} = \mathrm{Min}\left\{1, \ (k_M/q_o)(2-\omega_o/\omega_M)\right\} .$$

Combining (20), (27), (36) and (37), we obtain the expression

$$(39) \qquad P_{II}(\underline{q}_o) = \frac{\hbar\Omega_c \gamma^2 \omega_c n_o (n_{A1}+1)(n_{A2}+1)}{27\pi(M_{opt} M_{acoust}^2)^{1/3} c_A^5} \int_{-m}^{m} \frac{\omega_{A1}^3 \omega_{A2}}{1-\cos\theta_{12}} \frac{\partial\cos\theta_{A1}}{\partial\mu} d\mu \, .$$

We must note that P_{II} depends on the order of Umklapp through $\underline{q}_o$, which is equal to $\underline{k}_o$ or $\underline{k}_o - \underline{K}$, depending on whether we are dealing with a normal process (N), or an Umklapp process (U), which corresponds to the case $n_x = 1$ of Fig. 4. If we write $k_o = \kappa k_M$, then our approximate final expression for $P_{II}(\underline{q}_o)$ is

$$(40) \quad \left\{ \begin{array}{l} P_{II}(\underline{q}_o) = P_{II}(\kappa, \Lambda) = P^o \Pi_\Lambda(\kappa) n_o (n_{A1}+1)(n_{A2}+1); \qquad \Lambda = N, U \\[2ex] P^o = \dfrac{\hbar\Omega_c (\omega_o/c_A)^5 \gamma^2}{432\pi(M_{opt} M_{acoust}^2)^{1/3}} \\[3ex] \Pi_N(\kappa) = \left\{ \begin{array}{ll} 1 - \kappa^2/6 + \kappa^4/80; & 0 \leq \kappa \leq \kappa_o = 2(2\omega_M/\omega_o - 1) \\ (\kappa_o/\kappa)(1 - \kappa_o^2/6 + \kappa_o^4/80); & \kappa_o \leq \kappa \leq 1 \end{array} \right. \end{array} \right.$$

(40 cont'd)

$$\Pi_U(\kappa) = (\kappa_0/2-\kappa)(1-\kappa_0^2/6+\kappa_0^4/80); \quad 0 \leq \kappa \leq 1.$$

In practice, we are most interested in the total transition probability, representing the average of $P_{II}(\underline{k}_0, \Lambda)$ over all possible values of $\underline{k}_0$:

$$(41) \qquad P_{II,av}(\Lambda) = \left\{ \Omega_0/(2\pi)^3 \right\} \int P_{II}(\underline{k}_0, \Lambda)\, d^3\underline{k}_0, \qquad \Lambda = N, U.$$

The actual numerical values used for the various parameters are listed in Table I, and give the final result

$$(42) \qquad \left\{ \begin{aligned} &\frac{P_{II,av}(N)}{n_0(n_{A1}+1)(n_{A2}+1)} = 5.8 \times 10^{11} \text{ per sec} \\ &\frac{P_{II,av}(U)}{n_0(n_{A1}+1)(n_{A2}+1)} = 3.2 \times 10^{11} \text{ per sec} \end{aligned} \right.$$

for the mean transition probability per unit time of one optic phonon splitting up into two acoustic phonons under process II of equation (23).

6. The three-phonon process III

The purpose of this section is to sketch the calculation of the transition probability for process III of equation (24) and Fig. 2. The calculation will not be carried out in the same detail as that of the previous section for the process II, our object being to indicate that process III merely furnishes a small correction to process II. In particular, we shall not go into detail in examining the dependence of the matrix elements on $\underline{k}_0$, $\underline{k}_{A1}$, $\underline{k}_{A2}$, $\underline{k}_{A3}$, because our limited knowledge of the coefficients b(0;A1;A2) and c(0;A1;A2;A3) does not warrant it.

From (27), (31) and (32), the transition probability for process III is

$$P_{III}(\underline{q}_0) = \int \frac{\hbar^2 |\tilde{c}(0;A1;A2;A3)|^2 n_0 (n_{A1}+1)(n_{A2}+1)(n_{A3}+1)\,\Omega_c^2 d^3\underline{k}_{A1} k_{A2} d\cos\theta_{A2} d\phi_{A2}}{9216\,(2\pi)^5 M_{opt} M^3_{acoust}\, c_A^3\, \omega_0 \omega_{A1}\, (1-\cos\theta_{23}) k_{A3}} . \tag{43}$$

We now have to integrate over $d^3\underline{k}_{A1}\ d\cos\theta_{A2} d\phi_{A2}$. Let us recall that $|c(0;A1;A2;A3)|^2$ depends on these quantities in some unknown but complicated way (cf. Section 3), and hence let us replace it by an average value. Similarly, let us put

$$\int \frac{\Omega_c^3 d^3\underline{k}_{A1}}{(2\pi)^3 \omega_{A1}} \int \frac{k_{A2} d\cos\theta_{A2} d\phi_{A2}}{k_{A3}(1-\cos\theta_{23})} \sim \frac{4\pi}{\omega_M} , \tag{44}$$

which gives

$$P_{III}(\underline{q}_0) \sim \frac{\hbar^2 \Omega_c |\tilde{c}(0;A1;A2;A3)|^2_{av} n_0 (n_{A1}+1)(n_{A2}+1)(n_{A3}+1)}{9216\, \pi\, M_{opt} M^3_{acoust}\, c_A^3\, \omega_0\, \omega_M} . \tag{45}$$

This may be compared with the corresponding result (40) for $P_{II}(q_0)$. At sufficiently low temperatures we may put

$$n_{A1} = n_{A2} = n_{A3} = 0, \tag{46}$$

as relatively few acoustic phonons will be excited initially. Then, disregarding numerical factors of order one, we have

$$\frac{P_{III}(\underline{q}_0)}{P_{II}(\underline{q}_0)} \sim \frac{|\tilde{c}(0;A1;A2;A3)|^2_{av}}{|b(0;A1;A2)|^2_{av}} \cdot \frac{\hbar}{16 M_{acoust} \omega_M} : \tag{47}$$

If we now make the substitutions (20), (28) for $b(\ldots)$, $\tilde{c}(\ldots)$, and put

$$\frac{n_{\bar{A}} + 1}{(\omega_0 - \omega_{A1} - \omega_{\bar{A}})\, \omega_{\bar{A}}\, M_{acoust}} \sim \frac{1}{\omega_M^2 M^2_{acoust}} \tag{48}$$

then

$$\frac{P_{III}(\underline{q}_0)}{P_{II}(\underline{q}_0)} \sim \frac{(1+\alpha/100)^2}{10} ; \qquad 0.1 \lesssim \alpha \lesssim 10; \tag{49}$$

this ratio is certainly very much less than one.

7. Discussion

The central numerical result of the present calculation is equation (42), which gives

$$P_{II,av} \sim 10^{12}\ \text{sec}^{-1} \tag{50}$$

at sufficiently low temperatures ($T \ll \hbar\omega_M/k$, so that $n_{A1} = n_{A2} = 0$ in the mean). We may compare this with ω_M, which gives some measure of the mean 'collision frequency' of atoms in the crystal. On this basis, therefore, we may say that the efficiency of thermal (acoustic) vibrations in de-exciting an optic mode is of order

$$P_{II,av}/\omega_M \sim 2 \times 10^{-2}\ . \tag{51}$$

Similar numerical values have been obtained earlier, both classically and quantum mechanically, by Pauli, Born, Blackman, Barnes, Brattain and Seitz, and Huang[7] in calculating the widths of infrared dispersion lines in crystals. The result (51) may also be compared with the same general range ($10^{-6} - 10^{-2}$) for the efficiency of de-excitation of molecular vibrations by collisions in gases[3].

A number of assumptions have been made in the calculation. One of these is that the perturbation expansion (8) converges. This seems to be entirely satisfactory; one knows that the cubic and higher order terms in the potential are not important at reasonably low temperatures, and this is certainly borne out by the calculations of Section 6.

The present choice of frequency spectrum is reasonable for an exploratory calculation like the present one, but it is certainly not particularly satisfactory for a substance such as NaCl. It would be adequate for a lattice of two kinds of atoms having very different masses, or for molecular crystals (which would be the case of real interest here). In those cases, however, one would generally have

$$\omega_0/\omega_M \sim n, \quad n \gg 2, \tag{52}$$

so that n-th order transitions, and terms up to $V^{(n+1)}$ in the potential energy expansion (8a), would have to be considered in the calculation. This would give rise to technical problems in calculating transition probabilities, but more particularly to considerable new difficulties in estimating the magnitude of these terms in the potential.

Regarding the detailed expression used for the coefficients of the cubic and quartic potentials, equation (20) and especially (21)-(22) can hardly be regarded as a satisfactory approximation in the present case. More detailed calculations of the potential certainly appear to be called for.

One may ask why the present calculation has been referred to a very approximate three-dimensional model rather than to a better, one-dimensional one. The reason for this is that in three dimensions there are relatively many more high frequency modes than in a one-dimensional lattice, ($N(\omega)d\omega \sim d\omega$ in one dimension, $\omega^2 d\omega$ in three dimensions), and this is probably more important than the detail of the frequency spectrum.

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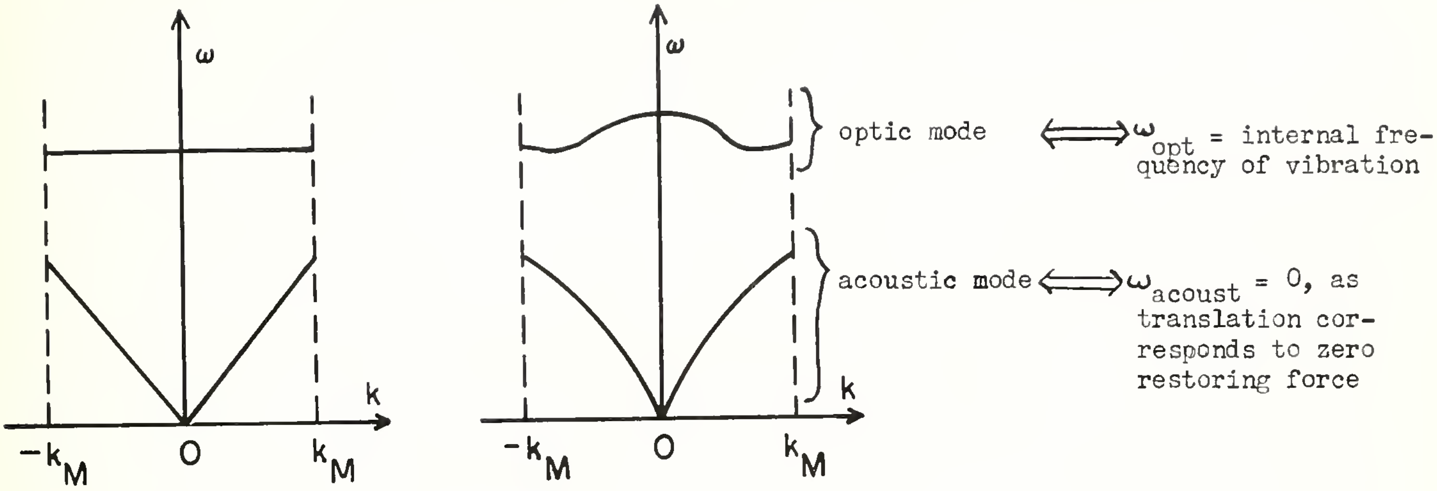
Table I. Numerical values of various constants for NaCl

Debye temperature, Θ_D	281 °K
$\omega_M = k\Theta_D/\hbar$	3.67×10^{13} sec^{-1}
ω_o	7.16×10^{13} sec^{-1}
interatomic distance, d	5.63×10^{-8} cm
Grueneisen constant, γ	1.61
Debye mean sound velocity, c_A	2.73×10^{5} cm/sec
M_{opt}	2.33×10^{-23} gm
M_{acoust}	9.71×10^{-23} gm
Ω_c	1.785×10^{-22} cm^3
K_o	.0526

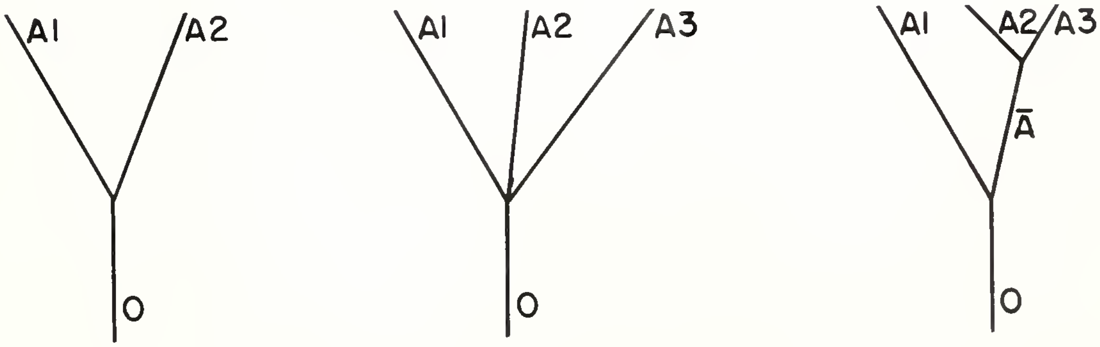

ω
k
$-k_M$
0
k_M
ω
optic mode
$\Longleftrightarrow \omega_{opt}$ = internal frequency of vibration
acoustic mode
$\Longleftrightarrow \omega_{acoust}$ = 0, as translation corresponds to zero restoring force
k
$-k_M$
0
k_M

Solid
(Debye-Einstein model)

Solid (exact)

Gas

Figure 1. Modes of vibration of a one-dimensional crystal lattice



Process II
$O \rightarrow A1 + A2$

Process IIIA

Process IIIB

$O \rightarrow A1 + A2 + A3$

Figure 2. Phonon-phonon collisions (time is measured increasing upwards)

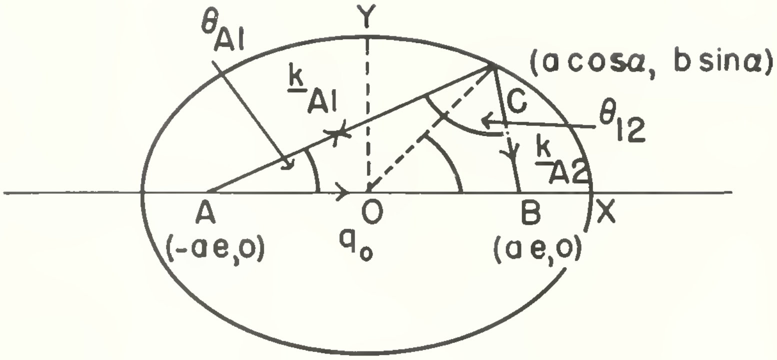
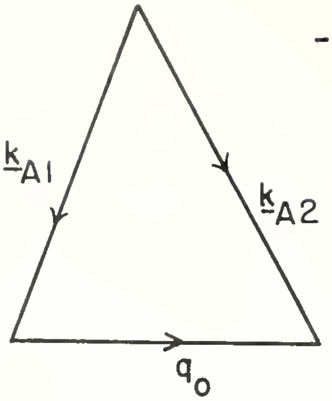
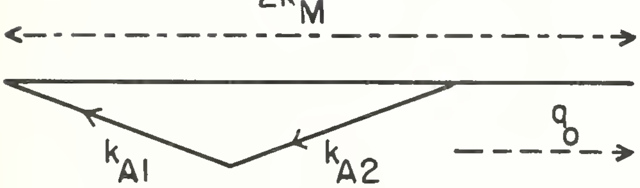


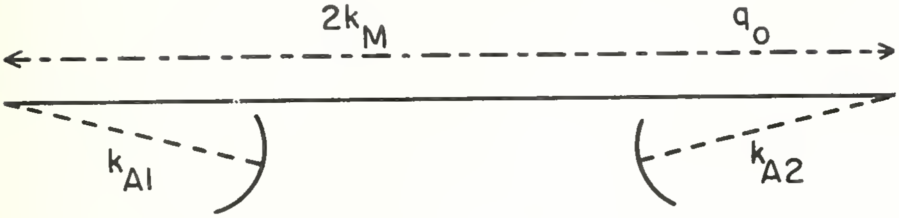
Figure 3. Energy-momentum conservation in two-phonon collisions



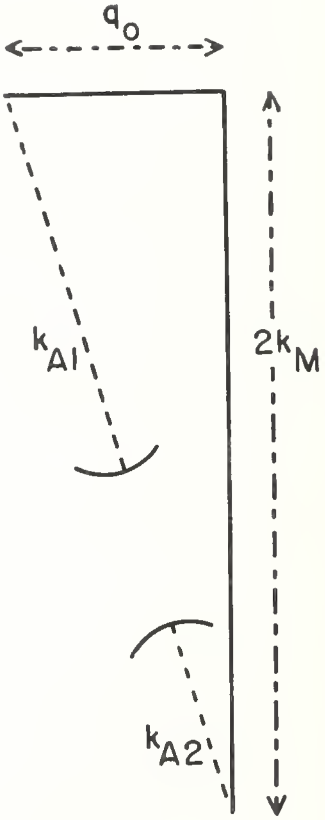
(i) Normal: no Umklapp



(ii) $n_x = 1$: Umklapp is possible



(iii) $n_x = -1$: no Umklapp possible



(iv) $n_y = \pm 1$: no Umklapp possible

Figure 4. Umklapp possibilities in two-phonon collisions

We take $|\underline{k}_{A1}|$, $|\underline{k}_{A2}| \sim 0.9\, k_M$, $|k_o| \sim 0.5\, k_M$,

$$\underline{k}_{A1} + \underline{k}_{A2} = \underline{k}_o - 2k_M\,(n_x, n_y, 0).$$

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